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(54) A METHOD FOR THE MANUFACTURE OF SODIUM CHLORIDE OR BRINE AND/OR CAUSTIC SODA AND ENGINEERING BRICK FROM ALUMINA PLANT RED MUD

(71) We, THE UNIVERSITY OF GUYANA, a body corporate as constituted by the Legislature of British Guiana Ordinance No. 6 of 1963, as amended by Ordinance No. 5 of 1965, of Turkeyen Campus, Greater Georgetown, Guyana (box 841), and GREGORY ONYEMAUWA IWU, a national of Nigeria, of 7 Enachu Street, Section K, Campbellville, Georgetown, Demerara, Guyana, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of sodium chloride or brine and/or caustic soda, and engineering brick from alumina plant red mud, a waste product in the manufacture of alumina or metal grade bauxite.

Alumina plant red mud presents a storage problem when discharged into ponds and pollution hazards when discharged into rivers or onto land employed for agricultural purposes. Hence the development of a technology that directly utilizes the alumina plant red mud is of economic as well as ecological significance. The main mineral ingredients of typical Guyana bauxites alumina plant red mud (dry solid basis) are Fe_2O_3 (12 wt %), SiO_2 (23 wt %), Al_2O_3 (31 wt %), TiO_2 (10 wt %) and Na_2O (12 wt %). Hitherto, when the Guyana bauxite alumina plant red mud or any alumina plant red mud for that matter, is treated with either sulphuric or hydrochloric acid solution it yields a solution containing the sulphates or the chlorides respectively of iron, aluminium, titanium and sodium. In the process of the present invention, sodium is selectively abstracted into solution from the alumina plant red mud, as sodium chloride, without bringing down or contaminating the solution with the chlorides of iron, titanium, silicon and aluminium. A concentrate of this solution is brine which is the basic material for the electrolytic production of caustic soda. The residual alumina plant red mud from the above, free from sodium, may be used for the production of an engineering brick. Hitherto, the relatively high proportion of soda in the alumina plant red mud, has rendered the latter unsuitable material for making an engineering brick.

According to the present invention, there is provided a process for the production of sodium chloride as brine from alumina plant red mud which comprises heating alumina plant red mud in the presence of hydrochloric acid, said hydrochloric acid being added to attain pH of 5.5 to 6, and separating the solids from the liquid phase. Solid sodium chloride can be recovered by evaporating the brine.

From a further aspect there is provided a method for producing engineering bricks (i.e. high load bearing) which comprises addition of kaolinitic clay to the residual solid from the reclamation process of the invention and firing at temperature between 1090 and 1150°C. Engineering bricks have a high compressive strength and are bricks intended for high load bearing applications.

Such bricks may have compressive strengths of 7×10^7 Nm^{-2} (approximately 10,000 psi) and average water absorption less than 1.4% by weight.

In the process of the invention alumina plant red mud which may already be in the form of slurry is used. Preferably the alumina plant red mud is dried at about 115°C, and then made into an aqueous slurry or mud. This mud is then heated, normally into the range 70—80°C and the pH adjusted to between 5.5 and 6 by the addition of hydrochloric acid, this addition being accompanied by vigorous agitation. The control of the addition of hydrochloric acid to attain the desired pH may be effected by means of a suspended titration or any other convenient means. Once this pH has been attained the suspension is allowed to cool and settle the solid and liquid phases separated by decantation or filtration.

The filtrate on evaporation to dryness usually yields on the average 12 parts by

weight of solid sodium chloride from 100 parts by weight of alumina plant red mud. A typical analysis of the solid is as follows:

sodium chloride 96—97%, calcium chloride 1.5—2%, sulphur 0.8—1% and phosporus 0.5—1%. When the solid is fused at 1000°C and re-analysed, it gives on the average 98—99% sodium chloride. Alternatively, if the filtrate is concentrated for example by evaporation to a volume of about 40% of its original volume, the resulting concentrate is a brine solution which would on electrolysis yield caustic soda, chlorine and hydrogen.

In the manufacture of bricks from the solid residue left after the extraction of the sodium species from the red mud, the residue is dried and pulverised to its original powdery form, and 80—90% by weight of this powder can be mixed thoroughly with 20 to 10% by weight respectively of a kaolinitic clay. (The average chemical composition of the kaolinitic clay was as follows, by weight: 70% SiO_2, 18% Al_2O_3, 6% Fe_2O_3, and 1% TiO_2. The X-ray diffraction and DTA studies on the kaolinitic clay shows the presence of kaolinitic quartz and micacious minerals.)

The mixture is made workable with water and the resulting slurry compacted and introduced into a wooden mould (e.g.

3.7 cm × 3.7 cm × 3.7 cm)

preferably lined with arborite. The mould is over-filled with the compacted mix, pressed down and levelled for example with a spatula. The bricks are dried and fired in any convenient manner. For example, they may be air-dried for about 24 hours and then dried at 150°C for about 3 days in a thermostatted oven, equipped with an exhaust fan. The bricks are fired for example in a thermostatted heavy duty furnace wherein they are heated at a temperature increasing from 200 to 1140°C at the rate of 50° per hour. The bricks are then heat-soaked or baked at 1140°C for eight hours.

The extraction of sodium chloride from alumina plant red mud is illustrated by the following example:

Example 1

To 100 parts by weight of alumina plant red mud, oven dried at 115°C, 500 parts by weight of water are added. The mixture is heated with vigorous and constant stirring to between 70—80°C. Within this temperature range, a suspended titration is performed on the mixture using 1 Molar solution of hydrochloric acid till the mixture attained a pH of between 5.5 and 6. To successfully carry out the suspended titration, the mixture must be continuously and vigorously stirred so as to have the particles of the mixture in a continuous suspension. When the mixture attained a pH of between 5.5—6, the titration is terminated, since only and all the sodium in the red mud is presumed to be in the solution. The mixture is left to cool. When the solid particles have settled down to the bottom of the reaction vessel as evidenced by a clear supernatant liquid, the latter is collected by decantation or filtration. The residue is washed with distilled water and the washings added to the filtrate. Washing of the residue is presumed complete when portions from the filtrate yield no crystals on evaporation to dryness. Four washings of the residue are usually sufficient.

The production of bricks according to the invention is illustrated by the following examples:

Example 2

90% of the solid separating from the aqueous phase after the treatment with hydrochloric acid according to Example 1 is mixed with 10% of kaolinitic clay and is then made into a brick cube of side 3.7 cm and fired to 1140°C and baked at this temperature for 8 hours; a brick with the following physical properties is obtained:

(a) Compressive strength:
8×10^7 Nm^{-2} (or approximately 12,000 p.s.i.) and
(b) Water absorption:
0.88% by weight.

Example 3

Following the procedures of Example 2 with 80% of the separated residue mixed with 20% kaolinitic clay a brick with the following physical properties is produced:

(a) Compressive strength:
7×10^7 Nm^{-2} (or approximately 10,000 p.s.i.) and
(b) Water absorption:
1.35% by weight.

WHAT WE CLAIM IS:—

1. A process for the production of sodium chloride as brine from alumina plant red mud which comprises heating alumina plant red mud in the presence of hydrochloric acid, said hydrochloric acid being added to attain a pH of 5.5 to 6, and separating the solids from the liquid phase.

2. A process according to Claim 1 wherein solid sodium chloride is recovered from the brine by evaporation thereof.

3. A process according to either of the preceding Claims wherein the treatment of alumina plant red mud is carried out at a temperature of from 70 to 80°C.

4. A process according to any one of the preceding Claims wherein alumina plant red mud is dried at a temperature of about 115°C,

and then made into an aqueous slurry prior to treatment with hydrochloric acid.

5. A process according to any of the preceding Claims wherein the separation of the solid and liquid phases is effected by decantation.

6. A method for producing engineering bricks which comprises the addition of kaolinitic clay to the residual solid from the process according to Claim 1, shaping and firing at temperature between 1090 and 1150°C.

7. A method for the treatment of alumina plant red mud substantially as described herein in Example 1.

8. A method for the production of bricks substantially as described herein in either of Examples 2 and 3.

9. Bricks whenever produced by the method of either of Claims 6 and 8.

10. Brine whenever produced by the process of any of Claims 1 to 5 and 7.

11. Caustic soda whenever obtained by concentration and electrolysis of brine as claimed in Claim 10.

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